



An advanced oxidation process by photoexcited heterogeneous sodium decatungstate for the degradation of drugs present in aqueous environment

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ABSTRACT

The ability of decatungstate anion ($W_{10}O_{32}^{4-}$) to photoproduce $OH\cdot$ radicals from water is retained when the polyoxoanion is immobilized on solid supports and can be exploited as a heterogeneous photocatalytic process aimed to water remediation. However, we show that interaction between $OH\cdot$ radicals and drug molecules depends on the physical chemical properties of the chosen support. In fact, we demonstrate that silica particles covered by decatungstate anions are not efficient in the degradation of carbamazepine and sulfamethoxazole (ubiquitous contaminants of natural waters) that are respectively neutral and negatively charged at operating pH of 6. On the contrary, entrapment of $W_{10}O_{32}^{4-}$ inside a mesoporous organosilica matrix leads to a heterogeneous photocatalytic system with proper characteristic of hydrophobicity. Organic molecules enter mesopores and easily leave the aqueous environment. Inside pores, the reaction between photoproduced $OH\cdot$ radicals is favored. Mono- and di-hydroxylated products precede fragmentation and degradation of the investigated drug.

1. Introduction

Water scarcity is a well-recognized challenge to the sustainable development of many countries that claims for further efforts to develop and improve water treatment technologies. It is therefore necessary the development of processes capable to ensure the total elimination of trace of organic contaminants from waters [1,2].

The use of advanced oxidation processes (AOPs) has been demonstrated to be a possible approach for the remediation of contaminated waters [3,4]. AOPs are based on the in situ production of free radical species, such as ($OH\cdot$), which being a strong oxidant characterized by a very high standard reduction potential ($E^\circ = +2.80$ V vs. SHE) rapidly oxidizes electron-rich organic compounds up to their mineralization [5]. Among the large variety of oxidation processes, photochemical methods offers the advantage of energy efficiency, rapidness and limited use of chemicals (oxidants), which together concur to the sustainability of the process [5]. In particular, photocatalysis with TiO_2 has been demonstrated to be an efficient method for the destruction of low amounts of water-soluble organic pollutants [6–8], even if other semiconductor materials, such as WO_3 , have been recently successfully utilized [9].

In water decontamination issue, the applicability of

polyoxotungstates for the degradation and mineralization of chlorophenols, chloroacetic acids and herbicide has been also explored [10,11]. Among polyoxotungstates, decatungstate anionic cluster has light absorption properties very similar to those of TiO_2 and for this similarity it can be considered a soluble analogue of the most employed semiconductor. In addition, it has been demonstrated that photoexcitation of $Na_4W_{10}O_{32}$ dissolved in water produces $OH\cdot$ radicals from water oxidation [12]. The interest for heterogeneous decatungstate photocatalyst in advanced oxidation processes framework has led to the development of several heterogenization procedures, such as impregnation on a solid support [13] and ion exchange [14,15]. Indeed, heterogeneous (photo)catalysis has the advantage of easy separation and recovery.

Recently, a heterogeneous photocatalytic system obtained by immobilization of the anionic decatungstate cluster on silica particles functionalized with $-NH_2$ groups has been employed for the degradation of some contaminants of emerging concerns in aqueous matrix [16]. It was proved that the photocatalytic system was efficient and recyclable. The degradation process is achieved by photoexcitation of heterogeneous decatungstate that results in the formation of $OH\cdot$ radicals as revealed by EPR spin trapping spectroscopy.

In addition, studies on the reaction mechanism of heterogeneous

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polyoxotungstates indicate that the selectivity and efficiency of these photocatalysts depend on the support characteristics. In general, pore structures, distributions of the active sites and hydrophilic–hydrophobic interactions with the substrate are key factors for the catalytic activity and selectivity of solid heterogeneous catalysts [17–19]. Therefore, the choice of support matrices is very important for highly efficient catalytic systems. In this paper, we show how support matrix properties can tune the degradation ability of immobilized decatungstate with respect to three target molecules in dilute aqueous solutions: propranolol, carbamazepine and sulfamethoxazole. These molecules are selected as probes since all of them are ubiquitous contaminants of natural waters. In particular, carbamazepine is a psychotropic drug, resistant to conventional wastewater treatment and sulfamethoxazole is an antimicrobial largely employed, which has been detected in surface and drinking waters [20].

Two different heterogeneous photocatalysts, obtained either by immobilization of $W_{10}O_{32}^{4-}$ by an ion exchange mechanism [16] or by encapsulation of the anionic cluster into a silicate structure [21], that were proved to be able to oxidize organic compounds, are here investigated.

In particular, their photocatalytic degradation activity with respect to contaminants of emerging concern is evaluated and the observed differences are related to both the support and the drug molecule physical chemical properties. EPR spin trapping technique and HPLC-MS analysis are employed to gain information about the operating degradative mechanism and the nature of reaction intermediates. In addition, composition and structural properties of the heterogeneous photocatalytic system are more deeply investigated. To the best of our knowledge, this is the first contribution where the photoactivity of decatungstate anion heterogenized on two different supports is compared, thus demonstrating that it is possible to tune the photocatalytic activity of the polyoxoanion by varying the chemical-physical properties of the support.

2. Experimental

2.1. Materials

Propranolol (PRP, purity 99.8%), carbamazepine (CBZ, purity 99.8%), sulfamethoxazole (SMX, purity 99.8%) and formic acid were purchased from Fluka (Fluka Chemie AG, Switzerland). Sodium hydroxide (Titolchimica, Rovigo, Italy), hydrochloric acid (Carlo Erba, Milano, Italy) of analytical grade were employed to adjust the pH of diluted drugs solutions. The pH was measured using an AMEL pHmeter (Milano, Italy). High-performance liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). The water was Milli-Q[®] grade (Millipore, MA, USA).

2.2. Photocatalysts preparation

Sodium decatungstate ($Na_4W_{10}O_{32}$) was synthesized following reported literature procedures [22,23]. The heterogeneous photocatalysts silica- $NH_3^+ / Na_3W_{10}O_{32}^-$ have been prepared carrying out the procedure recently published [16]. $Na_4W_{10}O_{32}/SiO_2/BTESE$ was prepared by simultaneous hydrolysis of tetraethylorthosilicate (TEOS, 23 mmol) and 1,2-bis(triethoxysilyl)ethane (BTESE, 2.3 mmol) in an acid aqueous solution of $Na_4W_{10}O_{32}$ [21]. The obtained material has a content of decatungstate of 0.33 mmol/g. The composition was determined by Inductively Coupled Plasma-Optical Emission Spectrometer ICP-OES (Perkin-Elmer Optima 3100 XL) equipped with an axial torch, segmented array charge coupled device (SCD) detector and Babington-type nebulizer with cyclonic spray chamber for sample introduction. Plasma conditions were: RF power of 1.40 kW applied to the plasma; 15 L min⁻¹ flow rate for plasma and 0.5 L min⁻¹ for auxiliary gas. Nebulizer gas flow rate was 0.65 L min⁻¹. Sample uptake was 1.5 mL min⁻¹ for each of three replicate scans. 0.5 g of samples were mineralized by microwave

acid digestion (HNO_3 , HF and H_3BO_3) at 200 °C and high pressure (200 psi), with 20 min dwell time.

At the end of preparation, UV–vis spectra of washing water aliquots showed that polyoxoanion was not released in the solution.

2.3. Photocatalytic experiments with homogeneous $Na_4W_{10}O_{32}$

An aerated aqueous solution (3 mL, final pH = 6) containing dissolved $Na_4W_{10}O_{32}$ (2×10^{-4} M) and the drug of interest ($C_0 = 10 \text{ mg L}^{-1}$) was put into a spectrophotometric cell (optical path 1 cm) and placed in front of a Hg medium pressure lamp (Helios Italquartz, 15 W cm⁻²). The solution is magnetically stirred and irradiation was carried out using a cut-off filter, placed between the lamp slit (1 cm x 3 cm) and the cuvette in order to select the suitable wavelength range (PRP, $\lambda > 330 \text{ nm}$, SMX $\lambda > 335 \text{ nm}$; CBZ, $\lambda > 300 \text{ nm}$). Selection of suitable cut off filter was performed in order to avoid direct photolysis of the drug compound. At the end of illumination, the sample was filtrated with 0.22 μm PVDF membrane filters Captiva Econofilter Agilent Technologies (Santa Clara, CA, USA) and HPLC analysis was performed. Samples containing dissolved decatungstate anion have been kept in the dark and then analyzed.

2.4. Photocatalytic experiments with heterogeneous $Na_4W_{10}O_{32}$

In a typical photocatalytic experiment, the optimal amount determined elsewhere [16,21] of silica- $NH_3^+ / Na_3W_{10}O_{32}^-$ (5 g/L) or of $Na_4W_{10}O_{32}/SiO_2/BTESE$ (8 g/L) was kept in suspension in aqueous solution (3 mL, pH = 6) containing the drug of interest ($C_0 = 10 \text{ mg L}^{-1}$) inside a spectrophotometric cell. Then, irradiation was carried out for the required period of time with the selected cut off filter (PRP, $\lambda > 330 \text{ nm}$, SMX $\lambda > 335 \text{ nm}$; CBZ, $\lambda > 300 \text{ nm}$) and at the end of irradiation the solution was analyzed as described above.

After irradiation, the solutions were centrifuged to separate the heterogeneous photocatalysts and UV–vis spectra have been recorded to evaluate leaching of decatungstate anion. Moreover, these solutions have been subsequently irradiated to establish eventual photoactivity of traces of decatungstate cluster, leached into the solution and not detected by spectrophotometric analysis.

Some photocatalytic experiments have been carried out to evaluate the stability of decatungstate on the support, by recovering $Na_4W_{10}O_{32}/SiO_2/BTESE$ (8 g/L) after the first photocatalytic experiment, washing with aliquots of acetonitrile and drying in the oven at 373 K for 60 min. The photocatalytic system has been reused in a second experiment, suspending it in an aqueous solution (3 mL, pH = 6) containing CBZ ($C_0 = 10 \text{ mg L}^{-1}$) and irradiated as described above. The irradiated solution was then analysed.

2.5. HPLC analysis

A HPLC/DAD (Waters, MA, USA pump: Waters 515, DAD: Waters PDA 996) was employed under isocratic elution conditions, reported in Table 2. The flow rate was 1 mL min⁻¹, while the column was thermostated at 25 °C. The column was 150 × 4.6 mm (Phenomenex, CA, USA) and packed with a C18 silica-based stationary phase with a particle diameter of 5 μm . The injection volume was 20 μL for all standards and samples.

2.6. HPLC/MS analysis

HPLC/MS analyses were carried out by means of Surveyor Plus micro-HPLC hyphenated to a linear ion trap mass spectrometer (LTQ XL Thermo Scientific, Waltham, MA, USA). The HPLC apparatus was composed of a solvent delivery system, a quaternary pump (including a membrane degasser) and an autosampler (including a thermostated column compartment). The LTQ system was equipped with an electrospray ionization (ESI) ion source. The mobile phase was obtained as

a mixture of ACN and formic acid 0.1% v/v: water formic acid 0.1% v/v. Chromatographic separation was performed under gradient elution conditions: 0–6 min 5% ACN, 6–14 min 5–70% ACN, 14–15 min 70% ACN, then held isocratically at 95% of ACN for 3 min before reconditioning the column. The flow rate was $100 \mu\text{L min}^{-1}$, while the column was thermostated at 25°C . The column was $50 \times 2.1 \text{ mm}$ (Restek, Bellefonte, PA, USA) packed with a C18 silica-based stationary phase with a particle diameter of $3 \mu\text{m}$. The injection volume was $5 \mu\text{L}$ for all standards and samples. MS experimental conditions were as follows: spray voltage 4 kV, capillary temperature 275°C , capillary voltage 11 V and tube lens 25 V for positive ESI conditions.

2.7. EPR-spin trapping experiments

EPR-spin trapping experiments were carried out with a Bruker ER200 MRD spectrometer equipped with a TE201 resonator (microwave frequency of 9.4 GHz). The homogeneous samples were aqueous solutions containing 5,5'-dimethylpyrroline N-oxide (DMPO, $5 \times 10^{-2} \text{ M}$) as spin trap and $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \times 10^{-4} \text{ M}$). In heterogeneous experiments, silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ was suspended in an analogous solution. When requested, CBZ ($C_0 = 10 \text{ mg L}^{-1}$) was introduced together with the spin trap. The samples were put into a flat quartz cell and directly irradiated in the EPR cavity with a medium pressure Hg lamp equipped with cut off filter ($\lambda > 300 \text{ nm}$). No signals were obtained in the dark or during irradiation of the solution in the absence of decatungstate.

2.8. XRD analysis

X-ray diffraction was used to verify the incorporation of BTESE on silica-based support. Powder patterns were measured on a Bruker D8 Advance Diffractometer equipped with a Sol-X detector, using $\text{Cu K}\alpha_{1,2}$ radiation in the $3\text{--}110^\circ 2\theta$ range and a counting time of 12 s/step. Table 2S reports reflection information for $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2/\text{BTESE}$ phase, where HKL are hkl , STOL is the value of $\sin\theta/\lambda$, TTH is the 2θ position of the reflection, FWHM is the full width at half maximum of the reflection, FOSQ is F_0^2 , SIG is an estimate of σF_0^2 , FOBS is F_0 . The GSAS LeBail computer program with the EXPGUI interface (Larson, A. C., & Von Dreele, R. B. General Structure Analysis System (GSAS); Los Alamos National Laboratory: Los Alamos, NM, 2000, 86–748).

3. Results and discussion

3.1. Sodium decatungstate heterogenized on modified silica particles (silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$)

We recently demonstrated that a robust and recyclable photocatalytic system can be obtained by immobilization of the anionic cluster on silica particles functionalized with $-\text{NH}_2$ groups [16]. Moreover, photoexcitation of heterogeneous decatungstate (5 g/L) suspended in aqueous solutions ($\text{pH} = 6$) containing one among levofloxacin or trimethoprim or atenolol ($C_0 = 10 \text{ mg/L}$) caused drug degradation mediated by $\text{OH}\cdot$ radicals, whose formation has been pointed out by EPR spin trapping spectroscopy [16].

With the aim of evaluating the wide scope of the found method, we decided both to confirm the observed performance by using propranolol (PRP), another β -blocker similar in structure to the previous studied atenolol, and to prove the photocatalytic method extending to other two drugs having different structure and physical chemical properties. In particular, we choose the antibiotic sulfamethoxazole (SMX, often used in combination with the studied trimethoprim) and the antidepressant carbamazepine (CBZ), which is known as a very recalcitrant drug. The degradation of each substrate is followed during irradiation time and it is expressed as ratio C/C_0 (where C is the drug concentration at a certain time and C_0 is the initial one). Interestingly, we observe (Fig. 1) that PRP behaves similarly to atenolol and after 3 h irradiation about 60–65% of degradation was obtained. On the contrary,

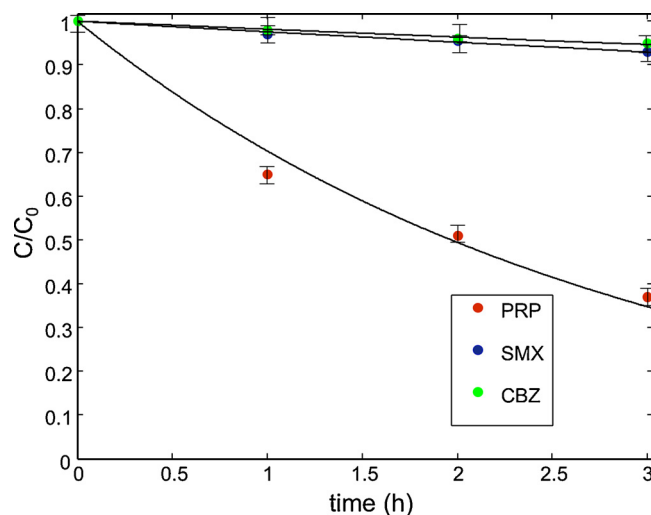


Fig. 1. Degradation kinetics of drugs by photoexcitation of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ (5 g/L) suspended in an aqueous solution ($\text{pH} 6$) containing propranolol (PRP), or sulfamethoxazole (SMX) or carbamazepine (CBZ). $C_0 = 10 \text{ mg/L}$. PRP, $\lambda > 330 \text{ nm}$; SMX $\lambda > 335 \text{ nm}$; CBZ, $\lambda > 300 \text{ nm}$.

irradiation of the silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ system does not cause any appreciable photocatalytic degradation of both SMX and CBZ.

On the basis of these results, we propose that the inefficient degradation of both SMX and CBZ could be due to one of the following factors: i) low photoactivity of the polyoxoanion with respect to these molecules; ii) scarce affinity of the catalyst support for the two drugs; iii) combination of factors ascribable to decatungstate and its support.

In order to evaluate the photocatalytic activity of decatungstate anion itself, experiments are carried out in homogeneous phase irradiating aqueous solutions containing dissolved $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \times 10^{-4} \text{ M}$) and CBZ, SMX or PRP ($C_0 = 10 \text{ mg/L}$). Obtained results are reported in Fig. 2 (circles), together with control experiments in which analogous samples are kept in the dark (squares).

It is shown that around 90% of starting CBZ and PRP are degraded after 60 min of illumination in the presence of homogeneous sodium decatungstate, and a lower degradation efficiency is obtained with SMX that is, however, photodegraded of about 60% in the first hour of irradiation. This decrease is attributable to the photocatalytic activity of $\text{W}_{10}\text{O}_{32}^{4-}$ since the decrease in the dark of CBZ, SMX or PRP never exceeds 10% (Fig. 2, squares).

Furthermore, EPR-spin trapping experiments support this statement.

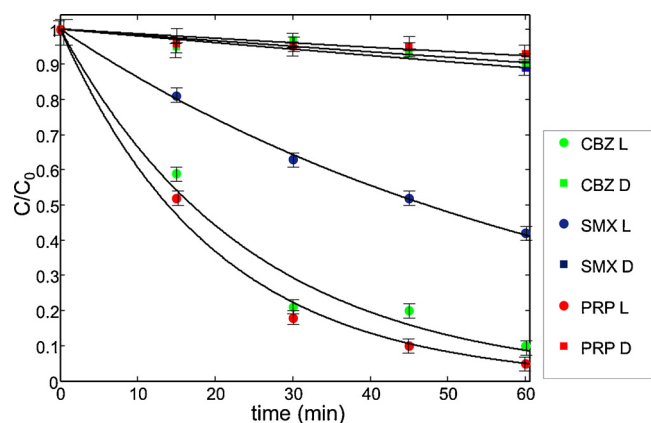


Fig. 2. Degradation kinetics of carbamazepine (CBZ), sulfamethoxazole (SMX) and propranolol (PRP) by photoexcitation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ($2 \times 10^{-4} \text{ M}$) dissolved in water at $\text{pH} 6$ (circles). Control experiments are carried out in the dark (squares). $C_0 = 10 \text{ mg L}^{-1}$. CBZ, $\lambda > 300 \text{ nm}$; SMX, $\lambda > 335 \text{ nm}$; PRP, $\lambda > 330 \text{ nm}$.

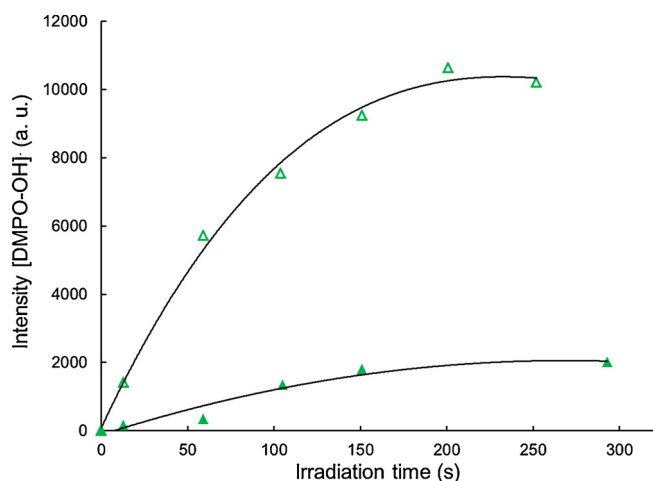
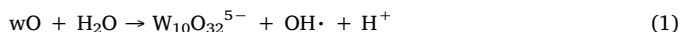


Fig. 3. Fixed-field signal intensity of the [DMPO-OH]• adduct in time upon irradiation ($\lambda > 300$ nm) of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ (2×10^{-4} M) dissolved in water containing DMPO (5×10^{-2} M): in the absence (full triangles) and in the presence (empty triangles) of CBZ (10 mg/L). Reported values are the mean of three repeated experiments. Errors do not exceed $\pm 10\%$.

In fact, photoexcitation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ dissolved in water in the presence of the spin trap DMPO causes the formation of a quartet 1:2:2:1 ($a_N = a_H = 14.8$ G) ascribable to the paramagnetic adduct [DMPO-OH]• in accordance to previous investigation [12]. As shown in Fig. 3, the intensity of this signal increases by increasing the irradiation time, showing that reactions:



efficiently occur. Interestingly, addition of CBZ (10 mg/L) to the solution causes an important decrease of [DMPO-OH]• signal. This could be an indication that CBZ competes with DMPO in the reaction with OH^\bullet radicals, and probably this reaction is the first step of the photocatalytic drug degradation pathway.

Analogous EPR spin trapping experiments carried out irradiating silica- $\text{NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ suspended in water containing DMPO show that the paramagnetic adduct [DMPO-OH]• is still formed, indicating that the primary photochemical process (reaction 1) that produces OH^\bullet radicals is operating also with the heterogeneous system. Contrarily to what observed for homogeneous decatungstate, the addition of CBZ does not cause any decrease in the intensity of the paramagnetic adduct (Fig. 4). This indicates that OH^\bullet radicals generated by photoexcited silica- $\text{NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ do not quickly react with CBZ, in agreement with the absence of degradation of this drug shown in Fig. 1. Possibly, CBZ does not adequately approach the surface of the heterogeneous photocatalyst where OH^\bullet radicals are produced or CBZ concentration in the solution in contact with the particle is insufficient to favor the reaction between them two.

The different behavior of silica- $\text{NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ with respect to the studied drugs can be tentatively rationalized considering their distribution diagrams (Fig. S1): at the operative pH of 6, while the β -blockers (PRP and atenolol, ATN) are mainly present in solution as cations, the same is not for CBZ and SMX. In fact, CBZ is in its neutral form and SMX presents an equilibrium between neutral and even negative form. Since the silica particles are covered by decatungstate anions, it can be supposed that immobilized decatungstate anions and CBZ or SMX are not sufficiently close each other, a needed requirement for the reaction between drug molecule and photogenerated OH^\bullet radicals.

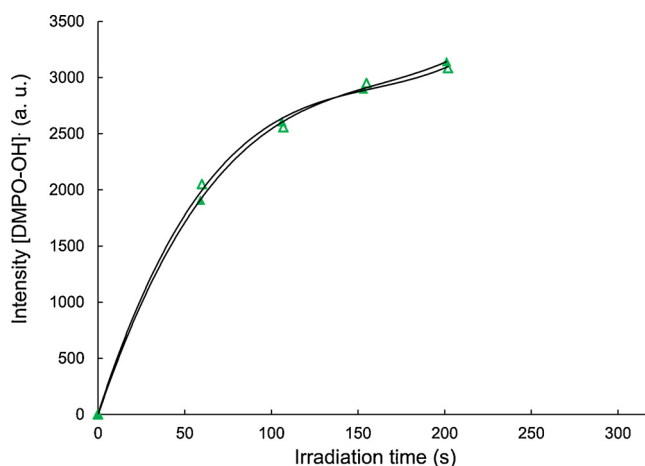


Fig. 4. Fixed-field signal intensity of the [DMPO-OH]• adduct in time upon irradiation ($\lambda > 300$ nm) of silica- $\text{NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ suspended in an aqueous solution containing DMPO (5×10^{-2} M): in the absence (full symbols) and in the presence of CBZ (10 mg/L) (empty symbols). Reported values are the mean of three repeated experiments. Errors do not exceed $\pm 5\%$.

3.2. Sodium decatungstate heterogenized on hydrophobic mesoporous silica support ($\text{SiO}_2/\text{BTESE} / \text{Na}_4\text{W}_{10}\text{O}_{32}$)

One of the main advantages of heterogeneous photocatalysis is the flexibility in choosing the support with the proper characteristics. Starting from the fact that silica- $\text{NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ is not able to perform efficient photocatalytic degradation of CBZ and SMX (Fig. 1), we thought that a heterogeneous photocatalyst obtained by direct hydrolysis of TEOS and of an organotrialkoxy silane (BTESE) should be hydrophobic enough to favor the approach of organic drugs dissolved in an aqueous matrix. Morphological features of $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ have been determined: we have checked that $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ employed in this research presents similar morphological characteristics to those of an analogous heterogeneous system previously used [21]. In particular, the specific surface area is roughly $700 \text{ m}^2 \text{ g}^{-1}$ and about 80% of total pore volume are classified as mesopores. Additionally, FTIR spectra clearly showed that organic fragments (coming from BTESE) and silica moieties are distributed within the framework and microgravimetric adsorption isotherms pointed out that $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ enhances adsorption of toluene vapors with respect to that of water [21]. To complete the characterization, XRD was used to determine $\text{Na}_4\text{W}_{10}\text{O}_{32}$ unit cell parameters starting from the CIF file deposited with the Cambridge Crystallographic Data Center under number CCDC 1548831. The $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2/\text{BTESE}$ refined XRD pattern is shown in Fig. 5.

From Fig. 5 the peaks at scattering angle (2θ) values of 16.52° , 25.57° , 34.22° and 35.04° were assigned to $\text{Na}_4\text{W}_{10}\text{O}_{32}$ respectively. The main crystallographic data and refinement results are as follows: triclinic crystal symmetry, space group $P_{\bar{1}}$, $a = 11.9532(6) \text{ \AA}$, $b = 12.2201(7) \text{ \AA}$, $c = 12.1898(8) \text{ \AA}$, $\alpha = 75.343^\circ(4)$, $\beta = 71.525^\circ(4)$, $\gamma = 88.083^\circ(5)$, cell volume = $1631.70(17) \text{ \AA}^3$. Values in parenthesis represent the standard deviations of the parameters computed on the basis of 8467 independent observations. Final reliability factors over the observed reflections $R_p = 0.0403$, $R_{wp} = 0.0535$, $\chi^2 = 1.029$ (where $R_p = \sum |Y_{io} - Y_{ic}| / \sum Y_{io}$; $R_{wp} = [\sum w_i(Y_{io} - Y_{ic})^2 / \sum w_i Y_{io}^2]^{0.5}$).

These data allows us to infer that decatungstate anion is not significantly modified during the synthesis of the heterogeneous system via hydrolysis of TEOS and of BTESE. In addition, XRD analysis shows that it is encapsulated inside the mesoporous network. Finally, the decatungstate content was determined by ICP-OES measurement (see par. 2.2).

As described in the Experimental Section, the synthesis process of $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ includes the hydrolysis of TEOS and of BTESE

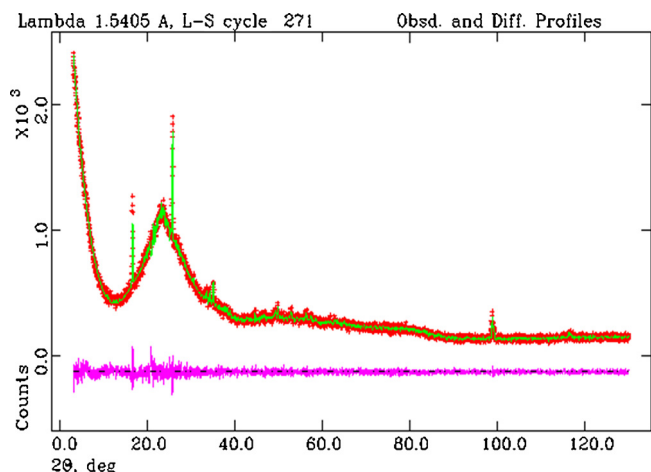


Fig. 5. Observed (red dotted line), calculated (green solid line) and difference (purple bottom line) X-ray powder diffraction patterns for $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2/\text{BTESE}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

in the presence of an acid solution of sodium decatungstate. Silanol groups ($\equiv\text{Si}-\text{OH}$) can be protonated in the acidic medium to form $\equiv\text{Si}-\text{OH}_2^+$. These groups, in turn, should act as counterions for decatungstate anion, that on the basis of XRD results is entirely encapsulated in the mesopores, leading to $(\equiv\text{Si}-\text{OH}_2^+)(\text{Na}_3\text{W}_{10}\text{O}_{32}^-)$ [24]. This strong interaction is confirmed by UV–vis spectra of washing water aliquots showing that polyoxoanion was not released in the solution.

Therefore, this heterogeneous photocatalytic system was used for attempting the degradation of CBZ and SMX and, in a typical experiment, $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$, suspended in an aqueous solution containing the drug of interest, is irradiated for a desired time (see Experimental section). In parallel, samples prepared in an analogous way are kept in the dark for the same period. The degradation of each substrate is expressed, as before, in terms of C/C_0 ratio vs time (Fig. 6).

One can observe that CBZ and SMX are now degraded upon photoexcitation of decatungstate. After 4 h illumination, more than 80% of CBZ and of SMX disappear from the aqueous solution. To verify the photoactivity of eventual leached polyoxoanion, the solution after one hour irradiation was separated from the heterogeneous photocatalyst, analyzed and then directly irradiated for an hour. The final analysis of these samples do not show a significant change ($< 2\%$) in remained

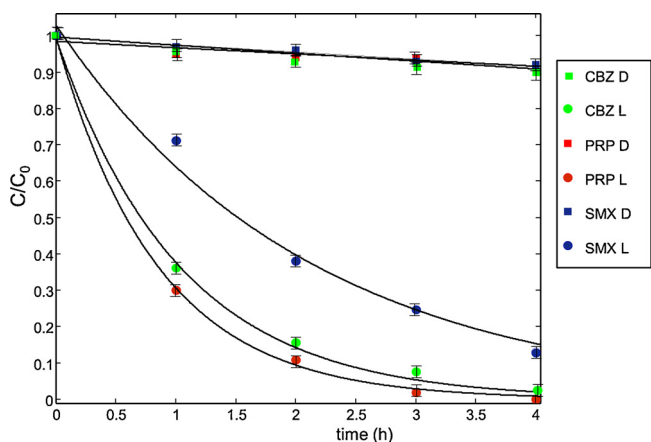


Fig. 6. Degradation kinetics of carbamazepine (CBZ), sulfamethoxazole (SMX) and propranolol (PRP) by photoexcitation of $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ (500 g L^{-1}) suspended in water at pH 6 (circles). Control experiments are carried out in the dark (squares). $C_0 = 10 \text{ mg L}^{-1}$. CBZ, $\lambda > 300 \text{ nm}$; SMX, $\lambda > 335 \text{ nm}$; PRP, $\lambda > 330 \text{ nm}$.

Table 1

Kinetic constants obtained by fitting the experimental data with a first order kinetic equation ($C/C_0 = \exp(-kt)$). Data in parenthesis are the confidence limits at 95% of probability.

Photocatalyst	drug	k (h^{-1})	R ²
$\text{Na}_4\text{W}_{10}\text{O}_{32}$ solution	CBZ	2.46 (2.10, 2.82)	0.9808
	PRP	2.94 (2.73, 3.05)	0.9934
	SMX	0.90 (0.89, 0.91)	0.9987
$\text{Silica-NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$	CBZ	0.024 (0.021, 0.027)	0.9837
	PRP	0.35 (0.28, 0.42)	0.9867
	SMX	0.021 (0.018, 0.024)	0.9881
$\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$	CBZ	0.97 (0.83, 1.11)	0.9977
	PRP	1.18 (1.08, 1.28)	0.9982
	SMX	0.48 (0.36, 0.60)	0.9825

drug concentration indicating that release of decatungstate into the solution is negligible. These results allow us to infer that the removal of CBZ and SMX occurs via the heterogeneous photocatalytic system employed. Moreover, the charge taken by the drug molecule at pH 6 (Fig. S1) that was an obstacle in the case of $\text{silica-NH}_3^+ / \text{Na}_3\text{W}_{10}\text{O}_{32}^-$ is overcome by this kind of support.

Concerning the stability of the material, $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ was recovered, washed with acetonitrile, dried at 373 K for 60 min and then used in a second experiment. The loss of activity in terms of both adsorption and photocatalytic degradation was within 10% after the two cycles, in agreement with the lack of release of anion during the experiment.

In Table 1 the kinetic constants obtained by fitting the data with a pseudo first order kinetic model are reported. A comparison can be made between homogeneous samples and heterogeneous experiments. One can additionally observe that SMX degradation kinetic is the slowest also with homogeneous sodium decatungstate, reinforcing the idea that the ionic charge of the drug molecule at pH 6 has a relevant role for the beginning of the oxidation process.

From these results, we suggest that the ability of $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ to photodegrade CBZ and SMX can be attributed to the hydrophobicity induced by BTESE to the heterogeneous photocatalytic system. From Table S1, CBZ and SMX are hydrophobic (see $\log k_{ow}$) and it has been already proved that they are adsorbed by high silica microporous material [25,26]. Moreover, the molecular dimensions are suitable with the pore sizes of the support where decatungstate anion is encapsulated. This can facilitate their approach to OH^\cdot radicals photoproduced nearby.

In addition $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ maintains a very good performance also in the degradation of PRP, showing that hydrophobicity introduced in the support does not preclude positively charged molecules from approaching the polyoxoanion (Fig. 1S). This result is particularly relevant since drugs photodegradation can be performed despite the form (charged or not) mainly present at the working conditions and answers to the requirement of general applicability.

3.3. HPLC/MS analysis

Degradation mechanism of drug molecules by $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ was investigated analyzing irradiated solution by HPLC-MS. Identification of the degradation byproducts was based on the analysis of the total ion current (TIC) and on the corresponding mass spectra. The identified intermediates for the case of SMX and of CBZ are reported in Tables 2 and 3 respectively.

The intermediate with 301 m/z corresponds to a monohydroxylation of the aromatic ring and a nitration of the amino group of SMX. The product with 283 m/z derives from the oxidation of the amino group to nitro derivative, whereas the intermediate with 270 m/z correspond to the hydroxylation of SMX aromatic ring. Oxidation of the isoxazole ring of 270 m/z results in the formation of 288 m/z and 228 m/z

Table 2

SMX: degradation intermediates, retention times, fragment ions and proposed structures.

Precursor Ion (m/z)	t _r (min)	MS ² (m/z)	Structure
301	9.18	177 133	
283	9.18	239 177 133	
270	10.25	206 228	
174	10.20	156	
190	3.76	158	
216	13.54	198	
288	14.46	270	
228	14.70		

Table 3

CBZ: degradation intermediates, retention times, fragment ions and proposed structures.

Precursor Ion (m/z)	t _r (min)	MS ² (m/z)	Structure
237.1	14.35	194.01 220.06	
251.1 253.1	12.3	208.0 210.0 236.0	
267.1	16.2	168 196.1 211.1	
271.1	9.6	210 253	

intermediate and the intermediate with 216 m/z can derive from the opening of the isoxazole ring of SMX. The cleavage of bond between isoxazole ring and the amine group of SMX, can generate the 174 m/z by-product. The compound with 190 m/z was identified as an

hydroxylated form of the amino group of 174 m/z derivative. Structures similar to those described were observed also in the photo-Fenton degradation of SMX [27].

From Table 2 it is seen that hydroxylation of SMX by hydroxyl radical (OH·) attack could be an important reaction for the subsequent degradation of SMX. Indeed, three mono-hydroxylated byproducts (i.e. 301 m/z, 270 m/z and 288 m/z) are revealed.

Mono and dihydroxylated intermediates were also identified in the CBZ degradation by photoexcited /SiO₂/BTESE/Na₄W₁₀O₃₂ catalyst in aqueous solution and they correspond to the intermediates 253 and 271 m/z respectively in Table 3. Further oxidation of both these compounds leads to the formation of 251 and 267 m/z intermediates. The detection of these intermediates indicates that hydroxylation and oxidation are the main reactions responsible for CBZ degradation.

On the basis of reported and previous results we propose a reaction mechanism for photoexcited /SiO₂/BTESE/Na₄W₁₀O₃₂ that can be considered general for pharmaceutical photocatalytic degradation. Photoexcitation of decatungstate anion dissolved or suspended in an aqueous environment causes the oxidation of water to OH· radicals [12], as shown in reaction 1. EPR spin trapping experiments and HPLC-MS point out that hydroxyl radicals attack drug molecules giving mono- or dihydroxylated intermediates. Their formation is the prelude to fragmentation.

4. Conclusions

The ability of photoexcited sodium decatungstate to oxidize water producing OH· radicals, already observed in homogeneous conditions, is kept also when the polyoxoanion is heterogenized on siliceous supports. In this paper, we demonstrate that support characteristics are of paramount importance when reaction between OH· radicals and the organic molecule is the first step of its degradative pathway. In particular, silica-NH₃⁺ / Na₃W₁₀O₃₂⁻ system, constituted by particles covered by decatungstate anions, is not efficient in the degradation of carbamazepine and sulfamethoxazole, which are neutral or negatively charged at the operating pH. On the contrary, entrapment of Na₄W₁₀O₃₂ inside a mesoporous organosilica matrix leads to a heterogeneous photocatalytic system with proper characteristic of hydrophobicity that is able to degrade not only carbamazepine and sulfamethoxazole but also all the other categories previously studied. In fact, the higher hydrophobicity of the organosilica support with respect to the aqueous environment favors adsorption of organic molecules, which enter the mesopores. Here, their proximity to photoproduced OH· radicals favors the hydroxylation of drug molecule. HPLC-MS investigation points out that mono- and di-hydroxylated products are formed and precede fragmentation pathways and degradation. Results obtained from the used independent techniques and methods allow us to formulate a general advanced oxidation process mechanism for the photocatalytic degradation of drug molecules by heterogeneous sodium decatungstate.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.08.015>.

References

- [1] B. Subedi, K. Kannan, Mass loading and removal of select illicit drugs in two wastewater treatment plants in New York state and estimation of illicit drug usage in communities through wastewater analysis, *Environ. Sci. Technol.* 48 (2014)

- 6661–6670.
- [2] M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water, *Environ. Sci. Technol.* 43 (2009) 597–603.
 - [3] M.N. Chong, A.K. Sharma, S. Burn, C.P. Saint, Feasibility study on the application of advanced oxidation technologies for decentralised wastewater treatment, *J. Clean. Prod.* 35 (2012) 230–238.
 - [4] J.L. Wang, L. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, *Critic. Rev. Environ. Sci. Technol.* 42 (2012) 251–325.
 - [5] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems, *J. Photochem. Photobiol. C: Photochem. Rev.* 9 (2008) 1–12 and references therein.
 - [6] M. Addamo, V. Augugliaro, A. Di Paola, E. Garcia-Lopez, V. Loddo, G. Marci, Removal of drugs in aqueous systems by photoassisted degradation, *J. Appl. Electrochem.* 35 (2005) 765–774.
 - [7] L.A. Ioannou, E. Hapeshi, M.I. Vasquez, D. Mantzavinos, D. Fatta-Kassinos, Solar/ TiO_2 photocatalytic decomposition of β -blockers atenolol and propranolol in water and wastewater, *Sol. Energy* 85 (2011) 1915–1926.
 - [8] L. Haroune, M. Salaun, A. Menard, C.Y. Legault, J.P. Bellenger, Photocatalytic degradation of carbamazepine and three derivatives using TiO_2 and ZnO: effect of pH, ionic strength, and natural organic matter, *Sci. Total Environ.* 475 (2014) 16–22.
 - [9] G. Longobucco, L. Pasti, A. Molinari, N. Marchetti, S. Caramori, V. Cristino, R. Boaretto, C.A. Bignozzi, Photoelectrochemical mineralization of emerging contaminants at porous WO_3 interfaces, *Appl. Catal. B: Environ.* 204 (2017) 273–282.
 - [10] P. Kormali, D. Dimotikali, D. Tsipi, A. Hiskia, E. Papaconstantinou, Photolytic and photocatalytic decomposition of fenitrothion by $\text{PW}_{12}\text{O}_{40}^{3-}$ and TiO_2 : a comparative study, *Appl. Catal. B: Environ.* 48 (2004) 175–183.
 - [11] P. Kormali, A. Troupis, T. Triantis, A. Hiskia, E. Papaconstantinou, Photocatalysis by polyoxometallates and TiO_2 : a comparative study, *Catal. Today* 124 (2007) 149–155.
 - [12] A. Molinari, R. Argazzi, A. Maldotti, Photocatalysis with $\text{Na}_4\text{W}_{10}\text{O}_{32}$ in water system: formation and reactivity of OH^\bullet radicals, *J. Mol. Catal. A Chem.* 372 (2013) 23–28.
 - [13] A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani, G. Sartori, Immobilization of (n-Bu₄N)₄W₁₀O₃₂ on mesoporous MCM-41 and amorphous silicas for photocatalytic oxidation of cycloalkanes with molecular oxygen, *J. Catal.* 209 (2002) 210–216.
 - [14] E.S. Da Silva, V. Prevot, C. Forano, P. Wong-Wah Chung, H.D. Burrows, M. Sarakha, Heterogeneous photocatalytic degradation of pesticides using decatungstate intercalated macroporous layered double hydroxides, *Environ. Sci. Pollut. Res.* 21 (2014) 11218–11227.
 - [15] A. Molinari, G. Varani, E. Polo, S. Vaccari, A. Maldotti, Photocatalytic and catalytic activity of heterogenized W₁₀O₃₂ – in the bromide-assisted bromination of arenes and alkenes in the presence of oxygen, *J. Mol. Catal. A Chem.* 262 (2007) 156–163.
 - [16] A. Molinari, E. Sarti, N. Marchetti, L. Pasti, Degradation of emerging concern contaminants in water by heterogeneous photocatalysis with $\text{Na}_4\text{W}_{10}\text{O}_{32}$, *Appl. Catal. B: Environ.* 203 (2017) 9–17.
 - [17] S.-S. Wang, G.-Y. Yang, Recent advances in polyoxometalate-catalyzed reactions, *Chem. Rev.* 115 (2015) 4893–4962.
 - [18] F. Zaera, The new materials science of catalysis: toward controlling selectivity by designing the structure of the active site, *J. Phys. Chem. Lett.* 1 (2010) 621–627.
 - [19] A. Maldotti, R. Amadelli, A. Molinari, M.G. Clerici, O. Kholdeeva (Eds.), *Liquid Phase Oxidation via Heterogeneous Catalysis*, Wiley, 2013, pp. 411–450 ch. 9.
 - [20] A.J. Ebele, M. Abou-Elwafa Abdallah, S. Harrad, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, *Emerg. Contam.* 3 (2017) 1–16.
 - [21] A. Molinari, G. Magnacca, G. Papazzoni, A. Maldotti, Hydrophobic $\text{W}_{10}\text{O}_{32}^{4-}$ /silica photocatalyst for toluene oxidation in water system, *Appl. Catal. B: Environ.* 138–139 (2013) 446–452.
 - [22] D.C. Duncan, T.C. Netzel, C.L. Hill, Early-time dynamics and reactivity of polyoxometalate excited states. identification of a short-lived LMCT excited state and a reactive long-lived charge-transfer intermediate following picosecond flash excitation of $[\text{W}_{10}\text{O}_{32}]^{4-}$ in acetonitrile, *Inorg. Chem.* 34 (1995) 4640–4646.
 - [23] F. Bigi, A. Corradini, C. Quarantelli, G. Sartori, Silica-bound decatungstates as heterogeneous catalysts for H_2O_2 activation in selective sulfide oxidation, *J. Catal.* 250 (2007) 222–230.
 - [24] Y. Guo, C. Hu, X. Wang, Y. Wang, E. Wang, Microporous decatungstates: synthesis and photochemical behavior, *Chem. Mater.* 13 (2001) 4058–4064.
 - [25] A. Martucci, L. Pasti, N. Marchetti, A. Cavazzini, F. Dondi, A. Alberti, Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites, *Microporous Mesoporous Mater.* 148 (2012) 174–183.
 - [26] S. Blasioli, A. Martucci, G. Paul, L. Gigli, M. Cossi, C.T. Johnston, L. Marchese, I. Braschi, Removal of sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: a study of the involved host–guest interactions by a combined structural, spectroscopic, and computational approach, *J. Colloid Interface Sci.* 419 (2014) 148–159.
 - [27] O. González, S. Carme, S. Esplugas, Sulfamethoxazole abatement by photo-Fenton: toxicity, inhibition and biodegradability assessment of intermediates, *J. Hazard. Mater.* 146 (2007) 459–464.